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Transformation Products of Iron(III) Hydroxide by Hydrolysis at Elevated Temperatures between 50 and 90°C

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Aqueous suspensions of gelatinous precipitates, prepared by mixing solutions of NaOH and one of iron(III) sulfate, chloride or nitrate in various ratios (R) of OH^-/Cl^- or NO_3^- , or $2\text{OH}^-/\text{SO}_4^{2-}$, were subjected to aging at temperatures between 50 and 90°C. All of the aging products thus obtained were examined by X ray powder diffraction, some further by chemical analysis, electron-microscopic observation and magnetic measurements. In alkaline media with $R > 1$, the gelatinous precipitates transform into $\alpha\text{-FeO(OH)}$ with or without $\alpha\text{-Fe}_2\text{O}_3$ depending on the aging temperature. For $R < 1$, the gelatinous precipitates dissolve into the acidic media and precipitates of $\alpha\text{-}$, $\beta\text{-FeO(OH)}$, $\alpha\text{-Fe}_2\text{O}_3$ and $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ are gradually formed depending on the aging temperature and the kind and concentration of the acid anion present. When LiOH is used as a precipitant in place of NaOH, the transformation into a ferromagnetic precipitate, LiFe_5O_8 , takes place in an alkaline medium at 50°C regardless of the kind of acid anion, whereas a basic iron sulfate can scarcely be formed in the acidic media. A variety of product formation in the acidic media can be explained on the basis of hydrolysis of iron(III) polynuclear complexes present in the media prior to the formation of precipitates.

KEY WORDS: Aging / Iron(III) hydroxide sulfates /
Iron(III) oxide hydroxides / Particle shapes /

INTRODUCTION

When an alkaline solution is added to an iron(III) salt solution, a brownish and gelatinous substance usually called iron(III) hydroxide is formed. The properties of the gelatinous precipitates, prepared by mixing solutions of aqueous ammonia and iron(III) nitrate, had earlier been studied closely by Giessen.¹⁾ The gelatinous precipitate is stable in a neutral medium,¹⁾ but unstable in an acidic or alkaline medium.²⁻⁷⁾

It has been known that the gelatinous precipitate transforms into $\alpha\text{-FeO(OH)}$ or $\alpha\text{-Fe}_2\text{O}_3$ in an alkaline medium depending on the aging temperature and that the temperature at which the formation of $\alpha\text{-Fe}_2\text{O}_3$ begins is governed by the aging conditions.²⁻⁴⁾

It has been also known that the gelatinous precipitate in an acidic medium at room temperature forms $\beta\text{-FeO(OH)}$ in the presence of Cl^- ion^{5,6)} or $\alpha\text{-FeO(OH)}$ with or without $\gamma\text{-FeO(OH)}$ in the presence of ClO_4^- ion.⁶⁾ It had also been reported that iron(III) basic sulfates, consisting of iron(III) sulfate and hydroxide, were formed in the

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presence of SO_4^{2-} ion.⁷⁾

In order to clarify the mechanism of the formation of each product, more systematic experiments were necessary. In this paper, our experimental results for the transformation products, obtained at elevated temperatures between 50 and 90°C of the gelatinous precipitates in acidic or alkaline media containing sulfate, chloride or nitrate, will be reported.

EXPERIMENTAL

The starting suspensions of the gelatinous precipitates of iron(III) hydroxide were prepared by adding a NaOH solution to an acidic solution of one of iron(III) sulfate, chloride or nitrate (each of analytical grade). A number of suspensions, varying in the ratios of OH^-/Cl^- or NO_3^- , or $2\text{OH}^-/\text{SO}_4^{2-}(\text{R})$ and in the iron ion concentration, were prepared. A series of suspensions were also prepared using LiOH as a precipitant in place of NaOH.

Stirring the suspension by air bubbling was found to be extremely helpful in accelerating the speed of aging the gelatinous precipitate as compared with the conventional magnetic or mechanical stirring method. Each suspension was diluted with water to 3L* in a 4L flask equipped with five inlet necks for insertion of a temperature regulator, a thermometer, a reflux condenser, an electrode pH meter and an air introducing tube. The construction of the flask was elsewhere specified.⁸⁾

The suspension was rapidly heated to a desired temperature and then stirred by bubbling air into it at a constant rate of 200L/h for 50h. The air from which carbon oxides had been removed by washing with a KOH solution was used for stirring the suspension. During the aging the temperature of suspension was kept constant.

The aging products were filtered through filter paper, washed with water, treated with acetone, and then dried at 100°C. All powdery samples thus obtained were examined by the X ray powder diffraction method using Mn filtered $\text{FeK}\alpha$ radiation, some by the electronmicroscopic observation and magnetic measurement at room temperature using a magnetic torsion balance. The magnetic susceptibility, χ , of all samples which had undergone the magnetic measurement did not exhibit any magnetic field dependence in the range 1 to 10kOe. The mean particle sizes of α - or β - $\text{FeO}(\text{OH})$ existing with or without another substance in the samples were estimated from the half broadening of X ray diffraction peaks.

RESULTS AND DISCUSSION

Processes of Transformation. Table I gives aging products and their physical properties when the suspensions with various R values, containing 0.07M** $\text{Fe}_2(\text{SO}_4)_3$ were subjected to aging at 50°C. As indicated in the table, the gelatinous precipitate, formed by mixing solutions of NaOH and $\text{Fe}_2(\text{SO}_4)_3$ at $\text{R}=1$, was chemically stable in a nearly neutral medium, the aging product being superparamagnetic. However, any gelatinous precipitate was very unstable in an acidic or alkaline medium and easily transformed

* $L=\text{dm}^3$.

** $\text{M}=\text{mol dm}^{-3}$

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Table I. Transformation Products of Gelatinous Precipitates in Suspension Media with Various R Values.

R	pH	Product	$\chi \cdot 10^{-6}(\text{emu/g})$	Particle sizes(\AA)		
				(110)	(130)	(111)
0.43	2.1 \rightarrow 1.9	a mixture*	54	90	—	—
0.68	2.3 \rightarrow 2.2	$\alpha\text{-FeO(OH)}$	53	60	—	—
0.85	2.9 \rightarrow 2.3	$\alpha\text{-FeO(OH)}$	53	60	—	—
1.0	9.1 \rightarrow 7.8	amorphous	180	—	—	—
2.0	12	$\alpha\text{-FeO(OH)}$	62	500	500	400

* $\alpha\text{-FeO(OH)}$ and $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$.

into a crystalline precipitate by aging. It was found by X ray analysis to consist of $\alpha\text{-FeO(OH)}$ with or without another substance having the same crystal structure as that of $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$.⁹⁾ The process of transformation in the alkaline medium could be visually observed to differ from that in the acidic media. In the course of transformation in the alkaline medium with $R=2$, 100 mL samples of the suspension were taken out after 0, 5 and 20h. After filtration, each separated precipitate was washed with water, treated with acetone and dried at 50°C in air. Examinations of these three samples indicated that the initial brownish color gradually turned yellowish with aging, the χ value decreased to 66×10^{-6} emu/g with an increase in the particle size perpendicular to the (110) plane of $\alpha\text{-FeO(OH)}$ crystals to 500 \AA in 20h of aging time. On the other hand, the gelatinous precipitates formed for $0.43 \leq R \leq 0.85$ dissolved completely into the acidic media with aging and before long, yellowish precipitates were gradually formed.

Such transformation processes in acidic or alkaline media could be observed, irrespective of the kind of iron(III) salt as thereafter described.

Transformation in Alkaline Media. Three kinds of alkaline suspensions containing 0.08M $\text{Fe}_2(\text{SO}_4)_3$ were prepared by mixing solutions of NaOH and $\text{Fe}_2(\text{SO}_4)_3$ with $R=1, 2, 2.0$ and 3.0 and subjected to aging at 50 and 80°C . X ray examination demonstrated that whereas the aging products obtained at 50 and 80°C from the suspensions with $R=3.0$ consist of an amorphous substance and $\alpha\text{-Fe}_2\text{O}_3$ respectively, other products consist of $\alpha\text{-FeO(OH)}$. These results indicate that increasing the concentration of excess NaOH causes a retardation in the velocity of transformation into a crystalline precipitate and a lowering of the temperature for the formation of $\alpha\text{-Fe}_2\text{O}_3$.

The temperature for $\alpha\text{-Fe}_2\text{O}_3$ formation had been reported to depend on the pretreatment of the gelatinous precipitate before aging at high temperature.^{3b)} The same suspensions as mentioned above had been allowed to stay at room temperature for 50h before they were aged at temperatures between 50 and 90°C . It was found that all gelatinous precipitates in alkaline media ultimately transformed themselves into $\alpha\text{-FeO(OH)}$ without forming $\alpha\text{-Fe}_2\text{O}_3$.

Similar experiments were conducted with iron nitrate and chloride in place of iron (III) sulfate. Transformation into $\alpha\text{-FeO(OH)}$ or $\alpha\text{-Fe}_2\text{O}_3$ took place, but no particular differences could be noted in the formation conditions for $\alpha\text{-FeO(OH)}$ or $\alpha\text{-Fe}_2\text{O}_3$ in alkaline media. Electronmicrographs of some products consisting of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeO(OH)}$ obtained from alkaline media are shown in Figs. 1 and 2.

When LiOH was used as a precipitant in place of NaOH, the gelatinous precipitate

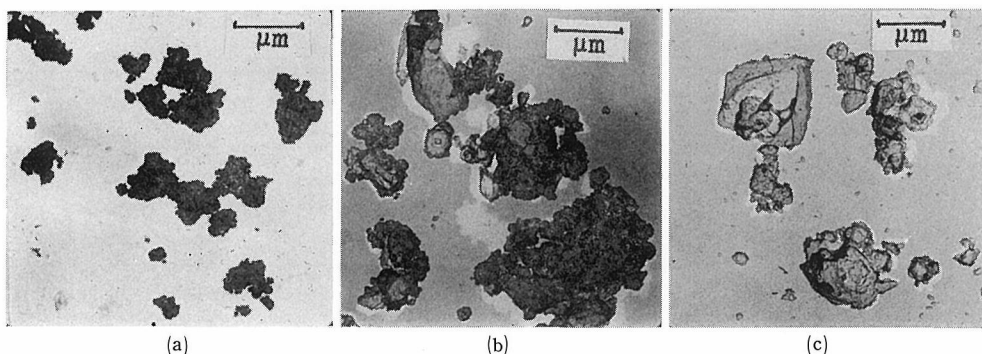


Fig. 1. Electronmicrographs of α - Fe_2O_3 precipitates prepared by aging at 80°C of alkaline suspensions with $R=3$, containing $0.08\text{M Fe}_2(\text{SO}_4)_3$ (a), 0.17M FeCl_3 (b) and $0.17\text{M Fe}(\text{NO}_3)_3$ (c). (b) and (c) were taken by the carbon replica method.

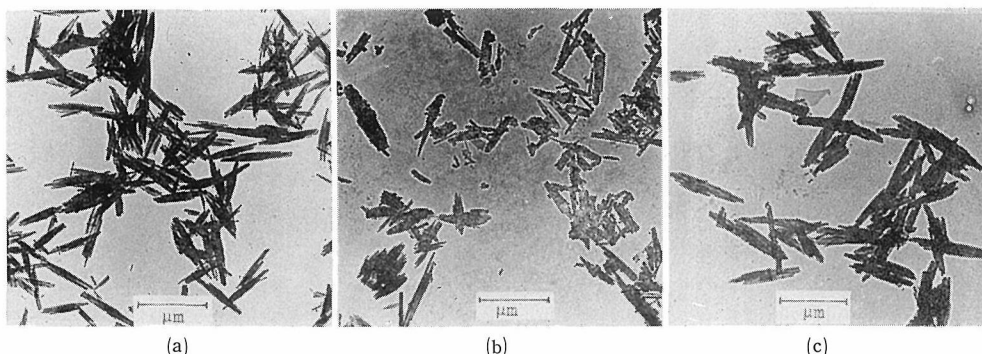


Fig. 2. Electronmicrographs of α - $\text{FeO}(\text{OH})$ precipitates prepared by aging at 80°C of alkaline suspensions with $R=1.7$, containing $0.2\text{M Fe}(\text{NO}_3)_3$ (a) and $0.1\text{M Fe}_2(\text{SO}_4)_3$ (b and c). (c) had been allowed to stand at room temperature for 50h before aging at 80°C .

in an alkaline medium transformed into a brownish ferromagnetic precipitate even at such low temperature as 50°C , irrespective of the kind of iron(III) salt used. The ferromagnetic precipitate was found by X ray examination to consist of spinel ferrite particles (LiFe_5O_8).

Transformation in Acidic Media. Four kinds of acidic suspensions with $R=0.4, 0.5, 0.75$ and 0.9 , each containing $0.14\text{M Fe}(\text{NO}_3)_3$, were subjected to aging at 50°C . The dissolution as visually detected of the gelatinous precipitates was followed by the formation of yellowish precipitates in the acidic media with $\text{pH}<2$ for $R\leq 0.75$. The duration of aging required for the precipitate formation became longer with increasing R . For the acidic medium with $R=0.9$, no visible precipitate was formed even after 50h. The yellowish precipitates were found to have the values of $50\times 10^{-6}\text{ emu/g}$ in χ and to consist of α - $\text{FeO}(\text{OH})$ particles, $50\text{--}60\text{ \AA}$ in size for the $[110]$ direction as a result of X ray examination.

Similar experiments were conducted using iron(III) chloride instead of iron(III) nitrate. But, precipitates formed at 0.14M FeCl_3 could not be isolated by filtration because of too fine particles. When acidic suspensions with $R=0.3, 0.6$, and 0.8 , each

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Table II. Effect of Aging Temperature on α -Fe₂O₃ Formation in Acidic Suspension Media Containing Nitrates.

Temp. (°C)	pH	Product	$\chi \cdot 10^{-6}$ (emu/g)	Particle size (Å) (110)
50	2.3 → 1.7	α -FeO(OH)	45	50
60	2.3 → 1.5	a mixture*	52	70
70	2.3 → 1.2	a mixture*	56	80
80	2.1 → 1.2	α -Fe ₂ O ₃	58	—

* α -Fe₂O₃ and α -FeO(OH).

Table III. Aging Products Obtained from Acidic Media Containing Sulfates at Different Temperatures.

Temp. (°C)	pH	Particle sizes (Å)		
		(110)	(130)	(111)
50	2.2 → 1.9	30	—	—
60	2.2 → 1.6	60	40	100
70	2.2 → 1.4	80	50	130
80	2.0 → 1.3	80	50	100

All products proved by X ray analysis to be a mixture of α -FeO(OH) and NaFe₃(SO₄)₂(OH)₆.

containing 0.6M FeCl₃, were aged at 50°C. The aging products were yellowish brown and found to have the χ values 40–70 × 10⁻⁶ emu/g and to consist of β -FeO(OH) particles, 40–50 Å in size for the [110] direction.

Acidic suspensions with R=0.5, each containing 0.16M Fe(NO₃)₃, were aged at several different temperatures. The experimental results are given in Table II. Reddish precipitates consisting of α -Fe₂O₃ or mixtures of α -FeO(OH) and α -Fe₂O₃ were formed at 60°C or higher as tabulated. With an increase in temperature, the precipitate formation was accelerated and both the α -Fe₂O₃ content and particle size increased.

Similar experiments were also conducted using FeCl₃ in place of Fe(NO₃)₃. When acidic suspensions with R=0.5, each containing 0.25M FeCl₃, were aged at temperatures 60, 70, 80 and 90°C, yellowish brown precipitates could be obtained by aging at 80 and 90°C, consisting of β -FeO(OH) particles with 70 Å size for the [110] direction.

When acidic suspensions with R=0.4, 0.6 and 0.8, containing 0.34 and 0.7M FeCl₃, were subjected to aging at 90°C, yellowish brown precipitates consisting of β -FeO(OH) particles with 90–100 Å in size for the [110] and reddish brown precipitates consisting of mixtures of α -Fe₂O₃ and β -FeO(OH) were formed depending only on R. The content of α -Fe₂O₃ in the mixture increased with increasing R.

Table III gives the experimental results obtained by subjecting acidic suspensions with R=0.4, each containing 0.08M Fe₂(SO₄)₃ to aging at different temperatures. All products were yellowish and found by X ray examination to be mixtures of NaFe₃(SO₄)₂(OH)₆ and α -FeO(OH). An increase in temperature resulted in an increase in the content of NaFe₃(SO₄)₂(OH)₆ as a result of accelerated hydrolysis.

Similar experiments were carried out by use of LiOH in place of NaOH in the presence of SO₄²⁻. The yellowish brown products obtained consisted of α -FeO(OH).

Note that under the present experimental conditions any basic iron(III) sulfate could not be detected by means of X ray examination.

It had been reported in our paper that hydrolysis of iron(III) ions formed at 70°C by slow oxidation of iron(II) ions in a strongly acidic sulfate solution causes the formation of $\text{Fe}_4\text{SO}_4(\text{OH})_{10} (= (\text{Fe}_2\text{O}_3)_2\text{SO}_3(\text{H}_2\text{O})_5)$ in the absence of Na^+ , K^+ , or NH_4^+ ion, whereas that of $(\text{Na}^+, \text{K}^+, \text{or } \text{NH}_4^+)\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ in the presence of Na^+ , K^+ , or NH_4^+ ion.¹⁰⁾ A paper reported that a precipitate of $\text{Fe}_3(\text{SO}_4)_2(\text{OH})_5 \cdot 2\text{H}_2\text{O}$ which is isomorphous with $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ can be formed by aging a strongly acidic solution at 80°C or higher, irrespective of the presence of Na^+ , K^+ , or NH_4^+ ion.¹¹⁾

Several samples, found by X ray and electronmicroscopic examinations to consist of a mixture of hexagonal or cubic particles of $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$, greater than 2–3 μm in size, and very fine needle like particles of $\alpha\text{-FeO}(\text{OH})$, were chosen from the products prepared at 50 and 80°C in the range $0.35 \leq R \leq 0.5$. After the samples had been dissolved in a dilute HCl solution by heating the contents of Na^+ and SO_4^{2-} ions were respectively determined by atomic absorption and gravimetric analysis. The results indicated that these samples contained Na^+ and SO_4^{2-} ions in the $\text{Na}^+/\text{SO}_4^{2-}$ ratio of 0.5.

Electronmicrographs of the particles of $\alpha\text{-FeO}(\text{OH})$ and $\beta\text{-FeO}(\text{OH})$ (sometimes in

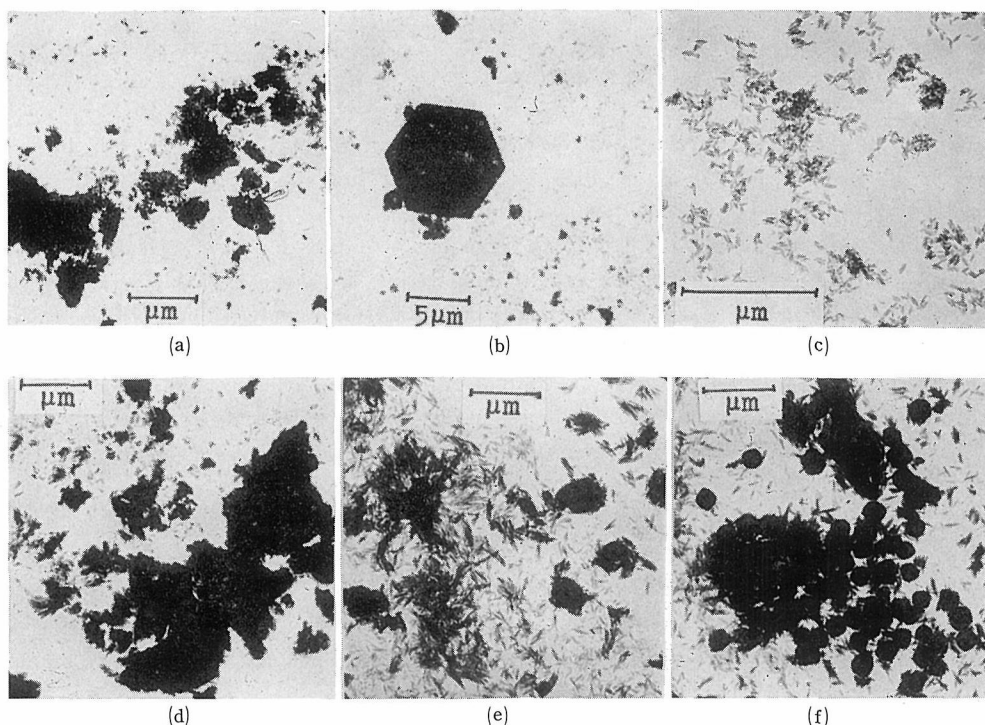


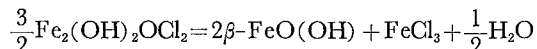
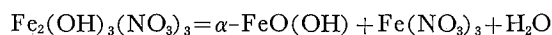
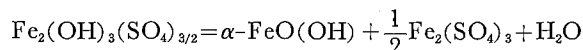
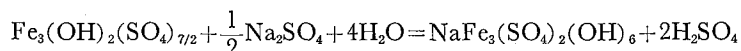
Fig. 3. Electronmicrographs of precipitates consisting of $\alpha\text{-FeO}(\text{OH})$ particles (a), a mixture of $\alpha\text{-FeO}(\text{OH})$ and $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ (b and c), $\beta\text{-FeO}(\text{OH})$ (d and e), and a mixture of $\beta\text{-FeO}(\text{OH})$ and $\alpha\text{-Fe}_2\text{O}_3$ (f). Precipitates of (a) and (b=c) prepared by aging at 80°C of an acidic suspension with $R=0.8$, containing 0.34M $\text{Fe}_2(\text{SO}_4)_3$ and by aging at 70°C of an acidic suspension with $R=0.4$, containing 0.08M $\text{Fe}_2(\text{SO}_4)_3$ respectively. (d), (e), and (f) prepared by aging at 70°C of an acidic suspension with $R=0.8$, containing 0.34M FeCl_3 , and at 90°C of acidic suspensions with $R=0.4$ and 0.8 respectively.

the form of a mixture) obtained from the acidic media are given in Fig. 3. Both kinds of particles were very fine or irregularly large as compared with the particles of α -, or β -FeO(OH) prepared by aging the alkaline suspensions (Fig. 2) or by hydrolysis through dilution or heating of iron(III) chloride solution.^{12,13)}

Since the needle-like particles of α - or β -FeO(OH) have a pronounced elongation in the [001] direction of its crystal structure, the mean particle size estimated from X ray diffraction examination is an approximate width-size. The large and irregular particles of α - and β -FeO(OH) shown in Fig. 3 (except for the large hexagonal NaFe₃(SO₄)₂(OH)₆ shown in (b) and the spherical α -Fe₂O₃ in (f)) each are considered to consist of very fine needle-like particles, less than 100 Å in width.

Mechanism of Precipitation in Acidic Media. Formation of a variety of products in the acidic media, as has been mentioned, is probably due to some differences in the composition and structure of the iron(III) ions present in the media prior to the precipitation. In our preceding paper, it was indicated that two kinds of polynuclear complexes consisting of a great number of [Fe₃(OH)₂]⁷⁺ and [Fe₂(OH)₃]³⁺ cations were formed in the presence of SO₄²⁻ ions by hydrolysis of the iron(III) ions and that the concentration of each kind formed was dependent on the pH. The polynuclear complex can only exist in the acidic media and it consists of either [Fe₂(OH)₃]³⁺ cations in the presence of NO₃⁻ ions or [Fe₂(OH)₂O]²⁺ cations in the presence of Cl⁻ ions.¹⁴⁾

From our experimental results, it can be inferred that the precipitation of each product in the acidic media takes place according to the formulas as follows: (where the H₂O ligands are abbreviated for simplicity)



As mentioned previously, with a rise in temperature the formation of α -Fe₂O₃ was accelerated. The formation in acidic media was found to be mainly governed by the kind of acid anion. α -Fe₂O₃ began to be formed at 60°C in the presence of NO₃⁻ ions and at 90°C in the presence of Cl⁻ ions. Whichever precipitate, α -Fe₂O₃ or FeO(OH), occurs in the same acidic medium due to the temperature difference may be attributed to the change in the structure of polynuclear complex as also discussed in our preceding paper.¹⁶⁾

The particles of α -FeO(OH), α -Fe₂O₃, and LiFe₅O₈ prepared in the alkaline suspensions were microscopically observed to have different shapes from each other. It is clear, therefore, that the formation of each precipitate takes place in the alkaline suspension medium. It would be difficult to clarify the mechanism for the precipitate formation in the alkaline suspension medium, impeded by the presence of precipitates.

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